

Simple physics of the partly pinned fluid systems

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In this paper, we consider some aspects of the physics of the partly pinned (PP) systems obtained by freezing in place particles in equilibrium bulk fluid configurations in the normal (nonglassy) state. We first discuss the configurational overlap and the disconnected density correlation functions, both in the homogeneous and heterogeneous cases, using the tools of the theory of adsorption in disordered porous solids. The relevant Ornstein-Zernike equations are derived, and asymptotic results valid in the regime where the perturbation due to the pinning process is small are obtained. Second, we consider the homogeneous PP lattice gas as a means to make contact between pinning processes in particle and spin systems and show that it can be straightforwardly mapped onto a random field Ising model with a strongly asymmetric bimodal distribution of the field. Possible implications of these results for studies of the glass transition based on PP systems are also discussed.

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I. INTRODUCTION

A number of recent theoretical and computational studies in the field of the glass transition have rested upon consideration of various types of so-called partly pinned (PP) systems, a class of models broadly characterized by their preparation protocol. Indeed, all PP systems have in common that they are generated from a simple statistical-mechanical model, such as a fluid or a spin assembly, in equilibrium under given thermodynamic conditions, by freezing (“pinning”) a subensemble of its constituents in individual states (particle positions or spin values) corresponding to a randomly chosen instantaneous configuration and letting the rest evolve under the influence of the frozen objects, all interactions and thermodynamic parameters being kept unchanged. Depending on the specific setup, such PP systems might be homogeneous, if the frozen objects are evenly distributed in the whole volume of the system, or heterogeneous, if they are located in a predefined region of space, the free ones being restricted to the complementary domain.

Because the systems from which they are prepared undergo thermal fluctuations, the PP systems always display quenched randomness, due to the frozen part. So, for any given starting statistical-mechanical model, set of thermodynamic parameters, and specific freezing procedure, a whole ensemble of PP systems is actually obtained. This leads one to focus on quantities averaged over this ensemble, as is standard in the study of quenched-disordered systems.¹ Thanks to the peculiar preparation protocol of the PP systems, the statistical properties of this ensemble are straightforwardly related to those of the starting model, and important simplifications follow.^{2–5} For instance, the sample-averaged configurational properties of a PP system exactly match those

of the system from which it derives. Also, the configuration of the free components immediately after the pinning step is automatically a representative equilibrium configuration of the corresponding PP sample. These features have been put to good use with studies in essentially three directions.

First, the PP fluid systems can be seen as models of confined fluids, with the frozen particles forming the confining environment. Accordingly, they have regularly appeared in computational studies of the dynamics of fluids in confinement,^{2,6–23} where their peculiar properties open up some interesting perspectives. Indeed, since the pinning process leaves the average configurational properties of a PP fluid system identical to those of the bulk fluid from which it is prepared, meaning in particular a perfectly flat average density profile and unperturbed pair correlations, one might argue that the study of PP systems gives access to the intrinsic dynamical effects of confinement, based on the fact that the possibility of interfering secondary effects originating in confinement-induced structural changes has been virtually eliminated by construction.^{2,9–11,22} Moreover, the immediate availability of a representative equilibrium configuration of the confined fluid just after the pinning step implies that it is not necessary to equilibrate the system after the confinement has been introduced. So, equilibrated bulk configurations are all that is required to produce PP fluid systems in equilibrium. This represents a decisive advantage when one is interested in the effect of confinement on the dynamics of glassforming liquids, which are already slow and challenging to investigate in the bulk and become much slower, sometimes by orders of magnitude, after pinning, so that they would be completely out of reach if equilibration was required. Thanks to this property, this pinning strategy has turned out particularly fruitful for the study of spatial dynamical correlations in confined glassy systems.^{2,9–12,19–21}

A second point of view is to consider the pinning process as a constraint imposed on the original statistical-

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mechanical model. It has been argued that such a constraint, whose characteristics are by construction fixed by the statistical properties of the system under study itself, represents a means to probe the existence of non-trivial static correlations in this system, without having to know their precise microscopic nature *a priori*. The basic idea is then to measure how the frozen degrees of freedom influence the accessible states of the free ones in the PP system, via the investigation of point-to-set correlations.^{5,24–29} This insight has motivated numerous computational studies of glassy systems in a variety of pinning geometries.^{4,20,21,30–42}

Finally, the PP systems can be considered as mere extensions of the statistical-mechanical model from which they derive, with an enlarged parameter space thanks to the addition as state variables of quantitative descriptors of the pinning process, such as the fraction of pinned constituents in the homogeneous case. Then, one can explore these extra dimensions with various models and theoretical tools, trying to unveil novel physical phenomena and possibly contrasting scenarios that would allow one to compare different approaches. Such studies have been recently undertaken for glassy systems, in the framework of the random first-order transition (RFOT) theory,^{43–47} of the mode-coupling theory (MCT),^{48,49} and of some dynamical facilitation models,⁵⁰ and in computer simulations of fluid models.^{15–17,51,52}

From this overview, it is manifest that a lot has been done to characterize the complex physics of the PP systems in the glassy regime. In comparison, their non-glassy physics is far less documented. This is precisely the focus of the present work, in which aspects of the theory of the PP systems deriving from normal fluid states are discussed. The motivation behind this study is that these systems represent a natural reference with respect to which the behavior of their glassy counterparts can be assessed. Thus, a better knowledge of their properties offers the prospect of pinpointing and maybe disentangling situations in which features that are mere consequences of the partial pinning approach possibly coexist and interfere with others originating in glassiness.

The paper is organized as follows. In Sec. II, basic properties of the PP systems needed in the following are reported. The main results of Ref. 3 on the homogeneous case are summarized, then extended to deal with heterogeneous pinning schemes. In Sec. III, the configurational overlap function introduced in the study of constrained systems is considered from the point of view of the theory of adsorption in disordered porous solids, in which many powerful tools have been developed to deal with simple fluids in contact with rigid quenched-disordered substrates.^{53–64} The homogeneous PP lattice gas is introduced in Sec. IV as a means to make contact between pinning processes in particle and spin systems. In both of the latter sections, possible implications of the results for studies of glassy PP systems are discussed. Finally, Sec. V is devoted to concluding remarks.

II. BASIC PROPERTIES OF THE PARTLY PINNED FLUID SYSTEMS

In this Section are reviewed simple properties of the PP fluid systems that are useful in the following.

As described in the Introduction, the PP fluid systems are generated from equilibrium bulk fluid configurations by pinning in place part of their particles, so that a quenched-disordered solid substrate is formed under whose influence evolve the remaining particles. We shall refer to the mobile and immobile particles as confined fluid (index f) and matrix (index m), respectively.

Although this is not strictly necessary, it is convenient to introduce a third species called template (index t), by reference to the templated-depleted systems studied by Van Tassel *et al.*^{65–70} Prior to pinning, the template refers to the particles of the original bulk system that will be left unpinned and can be seen as a precursor of the confined fluid. After pinning, it consists of immobile “ghost” particles marking the positions of these unpinned particles at the time of pinning. The template is essentially useful as a bookkeeping device in order to measure how the confined fluid configurations remain correlated with the bulk configurations from which the PP systems are prepared.

For simplicity, a grand-canonical description is used. Thus, the starting point is a one-component bulk fluid in a volume V at temperature T and activity z .⁷¹ As usual, we define $\beta = 1/k_B T$, k_B being Boltzmann’s constant. The probability density that this system consists of N particles located at $(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \equiv \mathbf{x}^N$ is

$$\mathcal{P}_{\text{bulk}}(N, \mathbf{x}^N) = \frac{z^N e^{-\beta V_{\text{bulk}}(N, \mathbf{x}^N)}}{\Xi_{\text{bulk}} N!}, \quad (1)$$

where $V_{\text{bulk}}(N, \mathbf{x}^N)$ denotes the potential energy. Ξ_{bulk} is the partition function, which, with the shorthand notation $\text{Tr} \dots \equiv \sum_{N=0}^{+\infty} \int d\mathbf{x}^N \dots$, reads

$$\Xi_{\text{bulk}} = \text{Tr} \frac{z^N e^{-\beta V_{\text{bulk}}(N, \mathbf{x}^N)}}{N!}. \quad (2)$$

A. Homogeneous systems

The ensemble of homogeneous PP fluid systems with average pinning fraction x is generated by imposing that, for every configuration of the fluid, each particle in the system can be frozen in place or not, with probabilities x and $1 - x$, respectively. The resulting joint probability density that one produces a matrix with N_m pinned particles located at $(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_{N_m}) \equiv \mathbf{q}^{N_m}$ while N_t unpinned particles are located at $(\mathbf{s}_1, \mathbf{s}_2, \dots, \mathbf{s}_{N_t}) \equiv \mathbf{s}^{N_t}$, is thus

$$\mathcal{P}_{\text{mt}}(N_m, \mathbf{q}^{N_m}, N_t, \mathbf{s}^{N_t}) = \frac{x^{N_m} (1-x)^{N_t} z^{N_m+N_t} e^{-\beta V_{\text{bulk}}(N_m+N_t, \mathbf{q}^{N_m}, \mathbf{s}^{N_t})}}{\Xi_{\text{bulk}} N_m! N_t!}. \quad (3)$$

It follows that the matrix configurations are distributed according to the probability density

$$\mathcal{P}_m(N_m, \mathbf{q}^{N_m}) = \text{Tr}_t \mathcal{P}_{mt}(N_m, \mathbf{q}^{N_m}, N_t, \mathbf{s}^{N_t}). \quad (4)$$

In order to now consider the confined fluid, it is necessary to recognize that Eq. (3) has the form suitable for a bulk ideal binary mixture in which the matrix and the template have activities xz and $(1-x)z$, respectively, and to separate the matrix-matrix, matrix-template, and template-template contributions to the potential energy prior to pinning, so that

$$V_{\text{bulk}}(N_m + N_t, \mathbf{q}^{N_m}, \mathbf{s}^{N_t}) = V_{\text{mm}}(N_m, \mathbf{q}^{N_m}) + V_{\text{mt}}(N_m, \mathbf{q}^{N_m}, N_t, \mathbf{s}^{N_t}) + V_{\text{tt}}(N_t, \mathbf{s}^{N_t}). \quad (5)$$

Then, since the confined fluid is assumed by construction to inherit its characteristics from the unpinned particles, its activity is taken equal to $(1-x)z$ and its potential energy to $V_{\text{mt}}(N_m, \mathbf{q}^{N_m}, N_f, \mathbf{r}^{N_f}) + V_{\text{tt}}(N_f, \mathbf{r}^{N_f})$, when N_f fluid particles located at $(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_f}) \equiv \mathbf{r}^{N_f}$ are in presence of a matrix with N_m particles located at \mathbf{q}^{N_m} . The probability density of such a fluid configuration depends parametrically on the matrix realization and reads

$$\mathcal{P}_f(N_f, \mathbf{r}^{N_f} | N_m, \mathbf{q}^{N_m}) = \frac{[(1-x)z]^{N_f} e^{-\beta[V_{\text{mt}}(N_m, \mathbf{q}^{N_m}, N_f, \mathbf{r}^{N_f}) + V_{\text{tt}}(N_f, \mathbf{r}^{N_f})]}}{\Xi_f(N_m, \mathbf{q}^{N_m}) N_f!}, \quad (6)$$

with the confined fluid partition function

$$\Xi_f(N_m, \mathbf{q}^{N_m}) = \text{Tr}_f \frac{[(1-x)z]^{N_f} e^{-\beta[V_{\text{mt}}(N_m, \mathbf{q}^{N_m}, N_f, \mathbf{r}^{N_f}) + V_{\text{tt}}(N_f, \mathbf{r}^{N_f})]}}{N_f!}. \quad (7)$$

These probability distributions obey the identity

$$\mathcal{P}_{mt}(N_m, \mathbf{q}^{N_m}, N_t, \mathbf{s}^{N_t}) \mathcal{P}_f(N_f, \mathbf{r}^{N_f} | N_m, \mathbf{q}^{N_m}) = \mathcal{P}_{mt}(N_m, \mathbf{q}^{N_m}, N_f, \mathbf{r}^{N_f}) \mathcal{P}_t(N_t, \mathbf{s}^{N_t} | N_m, \mathbf{q}^{N_m}), \quad (8)$$

from which the characteristic configurational properties of the PP systems follow.²⁻⁵ Thus, if ρ and $h(r)$ are the number density and total correlation function of the original bulk fluid, one gets for the corresponding quantities pertaining to the different species in the PP system,⁷²

$$\rho_m = x\rho, \quad (9a)$$

$$\rho_t = \rho_f = (1-x)\rho, \quad (9b)$$

$$h_{\text{mm}}(r) = h_{\text{mt}}(r) = h_{\text{mf}}(r) = h_{\text{tt}}(r) = h_{\text{ff}}(r) = h(r), \quad (9c)$$

$$h_{\text{tf}}(r) = h_{\text{dis}}(r). \quad (9d)$$

In the last equation, $h_{\text{dis}}(r)$ denotes the disconnected total correlation function that will be defined and discussed in detail in Sec. III.

B. Heterogeneous systems

In a heterogeneous PP fluid system, the volume occupied by the original bulk fluid is partitioned into two predefined complementary regions denoted by \mathcal{R} and $\overline{\mathcal{R}}$. In principle, they can be of arbitrary shape, but simple geometries are obviously favored in practical calculations.^{2,4,9-11,20-23,31-37,41,42} Then, the corresponding ensemble of PP systems is generated by imposing that, for every configuration of the fluid, the particles located in $\overline{\mathcal{R}}$ are pinned, while those in \mathcal{R} are left mobile.

A convenient mathematical tool encoding the region \mathcal{R} is its indicator or characteristic function, defined as

$$\chi_{\mathcal{R}}(\mathbf{x}) = \begin{cases} 1 & \text{if } \mathbf{x} \in \mathcal{R}, \\ 0 & \text{if } \mathbf{x} \notin \mathcal{R}. \end{cases} \quad (10)$$

The corresponding function for $\overline{\mathcal{R}}$ is obviously $\chi_{\overline{\mathcal{R}}}(\mathbf{x}) = 1 - \chi_{\mathcal{R}}(\mathbf{x})$.⁷³ Then, starting from Eq. (1) and according to the description of the heterogeneous pinning process, the joint probability density that one obtains a random substrate with N_m pinned particles located at \mathbf{q}^{N_m} while N_t unpinned particles are located at \mathbf{s}^{N_t} reads

$$\mathcal{P}_{mt}(N_m, \mathbf{q}^{N_m}, N_t, \mathbf{s}^{N_t}) = \frac{z^{N_m+N_t}}{\Xi_{\text{bulk}} N_m! N_t!} \times e^{-\beta V_{\text{bulk}}(N_m+N_t, \mathbf{q}^{N_m}, \mathbf{s}^{N_t})} \prod_{i=1}^{N_m} \chi_{\overline{\mathcal{R}}}(\mathbf{q}_i) \prod_{j=1}^{N_t} \chi_{\mathcal{R}}(\mathbf{s}_j). \quad (11)$$

Clearly, this probability density is identically zero if particles in $\overline{\mathcal{R}}$ are left unpinned and/or particles in \mathcal{R} are pinned. It therefore properly describes the targeted realization ensemble. Here as well, the probability distribution $\mathcal{P}_m(N_m, \mathbf{q}^{N_m})$ of the substrate configurations follows from Eq. (4).

The normalization condition of $\mathcal{P}_{mt}(N_m, \mathbf{q}^{N_m}, N_t, \mathbf{s}^{N_t})$ allows one to get

$$\Xi_{\text{bulk}} = \text{Tr}_m \text{Tr}_t \frac{z^{N_m+N_t}}{N_m! N_t!} \times e^{-\beta V_{\text{bulk}}(N_m+N_t, \mathbf{q}^{N_m}, \mathbf{s}^{N_t})} \prod_{i=1}^{N_m} \chi_{\overline{\mathcal{R}}}(\mathbf{q}_i) \prod_{j=1}^{N_t} \chi_{\mathcal{R}}(\mathbf{s}_j). \quad (12)$$

This corresponds to a rather unusual reformulation of the bulk system in terms of two subsystems, similar in spirit to the reformulation in terms of an ideal binary mixture in the homogeneous case.³ Here, since the indicator functions can be interpreted as Boltzmann factors corresponding to exclusion potentials, the two subsystems are spatially disjoint and the above expression of Ξ_{bulk} features the coexistence of a matrix component confined to $\overline{\mathcal{R}}$ with a template component confined to \mathcal{R} , both with activity z . A similar construction, but in the canonical ensemble, can be found in Ref. 4.

Once again, the confined fluid component in the PP system should inherit its characteristics from the template. So, with the same splitting of the potential energy

as in the homogeneous case, Eq. (5), the probability density of a fluid configuration with N_f particles at \mathbf{r}^{N_f} in presence of a substrate with N_m particles at \mathbf{q}^{N_m} reads

$$\mathcal{P}_f(N_f, \mathbf{r}^{N_f} | N_m, \mathbf{q}^{N_m}) = \frac{z^{N_f}}{\Xi_f(N_m, \mathbf{q}^{N_m}) N_f!} \times e^{-\beta[V_{mt}(N_m, \mathbf{q}^{N_m}, N_f, \mathbf{r}^{N_f}) + V_{tt}(N_f, \mathbf{r}^{N_f})]} \prod_{i=1}^{N_f} \chi_{\mathcal{R}}(\mathbf{r}_i), \quad (13)$$

with the confined fluid partition function

$$\Xi_f(N_m, \mathbf{q}^{N_m}) = \text{Tr}_f \frac{z^{N_f}}{N_f!} \times e^{-\beta[V_{mt}(N_m, \mathbf{q}^{N_m}, N_f, \mathbf{r}^{N_f}) + V_{tt}(N_f, \mathbf{r}^{N_f})]} \prod_{i=1}^{N_f} \chi_{\mathcal{R}}(\mathbf{r}_i). \quad (14)$$

It is straightforward to check that these probability distributions obey Eq. (8), so that the configurational identities of Ref. 3 (some of them have been first reported in Ref. 2) and their consequences can be readily extended to deal with the present type of systems. In particular, one gets for the density profiles and total correlation functions of the different species,⁷²

$$\rho_m(\mathbf{x}) = \chi_{\overline{\mathcal{R}}}(\mathbf{x})\rho, \quad (15a)$$

$$\rho_t(\mathbf{x}) = \rho_f(\mathbf{x}) = \chi_{\mathcal{R}}(\mathbf{x})\rho, \quad (15b)$$

$$h_{mm}(\mathbf{x}, \mathbf{y}) = h(|\mathbf{x} - \mathbf{y}|), \quad \mathbf{x}, \mathbf{y} \in \overline{\mathcal{R}}, \quad (15c)$$

$$h_{mt}(\mathbf{x}, \mathbf{y}) = h_{mf}(\mathbf{x}, \mathbf{y}) = h(|\mathbf{x} - \mathbf{y}|), \quad \mathbf{x} \in \overline{\mathcal{R}}, \mathbf{y} \in \mathcal{R}, \quad (15d)$$

$$h_{tt}(\mathbf{x}, \mathbf{y}) = h_{ff}(\mathbf{x}, \mathbf{y}) = h(|\mathbf{x} - \mathbf{y}|), \quad \mathbf{x}, \mathbf{y} \in \mathcal{R}, \quad (15e)$$

$$h_{tf}(\mathbf{x}, \mathbf{y}) = h_{dis}(\mathbf{x}, \mathbf{y}), \quad \mathbf{x}, \mathbf{y} \in \mathcal{R}, \quad (15f)$$

when the pinning process is performed on a bulk fluid with density ρ and total correlation function $h(r)$. Again, in the last equation, $h_{dis}(\mathbf{x}, \mathbf{y})$ denotes the disconnected total correlation function that will be studied in Sec. III.

We close this section with two remarks of practical use.

The present derivation clearly shows that the potential energy of the confined fluid in a heterogeneous PP system must contain an infinite contribution excluding the fluid particles from the matrix domain. Otherwise, without the corresponding product of $\chi_{\mathcal{R}}$ functions in $\mathcal{P}_f(N_f, \mathbf{r}^{N_f} | N_m, \mathbf{q}^{N_m})$, Eq. (8) is not obeyed and the ensuing characteristic configurational properties of the PP systems²⁻⁵ are lost. Such a contribution has been included in most computer simulation studies of heterogeneous PP systems on empirical grounds, in order to prevent the invasion of the substrate by the fluid particles. We find here that it is actually an integral part of the proper definition of a heterogeneous PP system.

The equality $h_{ff}(\mathbf{x}, \mathbf{y}) = h(|\mathbf{x} - \mathbf{y}|)$, $\mathbf{x}, \mathbf{y} \in \mathcal{R}$, is also worth a comment. Indeed, it is valid even if the points \mathbf{x} and \mathbf{y} belong to disconnected domains of \mathcal{R} , for instance, if they are separated from each other by a slab of pinned particles. It therefore implies that, in order to ensure the

statistical independence of the two interfacial subsystems located on each side of such a separation, a minimal requirement is in principle that this separation be thick enough to allow a complete decay of $h(|\mathbf{x} - \mathbf{y}|)$ between its boundaries. For dense fluids, this generically means thicknesses significantly larger than the mere range of the interaction potential.

III. OVERLAP AND DISCONNECTED CORRELATION FUNCTIONS IN THE NONGLASSY PARTLY PINNED FLUID SYSTEMS

In this Section, we consider the PP fluid systems from the point of view of the theory of simple fluids adsorbed on disordered substrates.⁵³⁻⁶⁴ We first show that the configurational overlap function is simply related to the disconnected two-point density and total correlation function. We then report some potentially interesting properties of the latter. Finally, we discuss how this knowledge could be useful in studies of glassy PP systems.

A. Measures of the one-body fluid density

As pointed out in the Introduction, the study of the PP fluid systems involves a disorder average over the matrix realizations in addition to the ordinary Boltzmann-Gibbs average which is then realization-dependent. It follows that specific types of configurational quantities, characteristic of random systems, come into play, as is already visible when dealing with the one-body fluid density, the most fundamental descriptor of the microscopic structure of a fluid in an inhomogeneous external potential.⁷¹

In any single sample of a PP fluid system, the randomly placed matrix particles are the sources of a very complex potential energy landscape in which the fluid is plunged. A fluid density profile results,

$$\rho_f[N_m, \mathbf{q}^{N_m}](\mathbf{x}) = \langle \hat{\rho}_f(\mathbf{x}; N_f, \mathbf{r}^{N_f}) \rangle_{N_m, \mathbf{q}^{N_m}}, \quad (16)$$

corresponding to the realization-dependent thermal average, denoted by $\langle \dots \rangle_{N_m, \mathbf{q}^{N_m}}$, of the microscopic one-body fluid density operator

$$\hat{\rho}_f(\mathbf{x}; N_f, \mathbf{r}^{N_f}) = \sum_{i=1}^{N_f} \delta(\mathbf{x} - \mathbf{r}_i). \quad (17)$$

Because of its parametric dependence on N_m and \mathbf{q}^{N_m} , $\rho_f[N_m, \mathbf{q}^{N_m}](\mathbf{x})$ is a highly complicated function of \mathbf{x} , with significant variations at the scale of the particle size.

From the point of view of the realization ensemble, $\rho_f[N_m, \mathbf{q}^{N_m}](\mathbf{x})$ appears as a scalar random field. A basic characterization of such an object is then through its mean (already considered in the previous section)

$$\rho_f(\mathbf{x}) = \overline{\rho_f[N_m, \mathbf{q}^{N_m}](\mathbf{x})} \quad (18)$$

and correlation function, often called the disconnected two-point density,

$$\rho_{\text{dis}}(\mathbf{x}, \mathbf{y}) = \overline{\rho_{\text{f}}[N_{\text{m}}, \mathbf{q}^{N_{\text{m}}}] (\mathbf{x}) \rho_{\text{f}}[N_{\text{m}}, \mathbf{q}^{N_{\text{m}}}] (\mathbf{y})}, \quad (19)$$

where $\overline{\cdots}$ denotes the disorder average. Through this averaging, these functions usually acquire a simple spatial dependence reflecting the symmetries of the pinning process. For instance, in the case of a homogeneous pinning, the average density profile $\rho_{\text{f}}(\mathbf{x})$ is actually independent of \mathbf{x} and $\rho_{\text{dis}}(\mathbf{x}, \mathbf{y})$ is a function of $|\mathbf{x} - \mathbf{y}|$ only.

Coarse-grained density fields might also be considered. Then, space is decomposed into cells, and the coarse-grained fluid density operator in cell i located at \mathbf{R}_i is defined as

$$\hat{n}_i(N_{\text{f}}, \mathbf{r}^{N_{\text{f}}}) = \int_{\text{cell } i} d\mathbf{u}_i \hat{\rho}_{\text{f}}(\mathbf{R}_i + \mathbf{u}_i; N_{\text{f}}, \mathbf{r}^{N_{\text{f}}}), \quad (20)$$

from which the analogues of the above functions are built,

$$n_i[N_{\text{m}}, \mathbf{q}^{N_{\text{m}}}] = \langle \hat{n}_i(N_{\text{f}}, \mathbf{r}^{N_{\text{f}}}) \rangle_{N_{\text{m}}, \mathbf{q}^{N_{\text{m}}}}, \quad (21)$$

$$n_i = \overline{n_i[N_{\text{m}}, \mathbf{q}^{N_{\text{m}}}]}, \quad (22)$$

$$n_{ij, \text{dis}} = \overline{n_i[N_{\text{m}}, \mathbf{q}^{N_{\text{m}}}] n_j[N_{\text{m}}, \mathbf{q}^{N_{\text{m}}}]}. \quad (23)$$

It is immediate that

$$n_{ij, \text{dis}} = \int_{\text{cell } i} d\mathbf{u}_i \int_{\text{cell } j} d\mathbf{u}_j \rho_{\text{dis}}(\mathbf{R}_i + \mathbf{u}_i, \mathbf{R}_j + \mathbf{u}_j), \quad (24)$$

and this equation is actually the starting point of a generic grid-based method that can be used to evaluate the disconnected two-point density in computer simulations⁷⁴ (see Ref. 75 for a similar analysis in reciprocal space). One can also check that $\hat{n}_i(N_{\text{f}}, \mathbf{r}^{N_{\text{f}}})$ is equal to the number of fluid particles in cell i in the fluid configuration $N_{\text{f}}, \mathbf{r}^{N_{\text{f}}}$. Therefore, the definition of $n_{ij, \text{dis}}$ for $i = j$ coincides, up to inessential factors, with the one of the static overlap computed in many simulation studies of PP fluid systems.^{4,20,21,31–38,41,51,52}

The ensuing result, that the overlap function is simply determined by the short-range part of the disconnected two-point density, is the generalization to arbitrary pinning geometries of the one reported in Ref. 39, where homogeneous PP fluid systems and a modified overlap function better suited for this case are considered.^{39,40,76} It is hardly spectacular, but has the merit of clearly showing that, for our purpose, the relevant aspect of the theory of adsorption in disordered porous media is its analysis of disconnected density correlations.

In this context, one usually deals with the so-called disconnected total correlation function $h_{\text{dis}}(\mathbf{x}, \mathbf{y})$, generically defined through

$$\rho_{\text{dis}}(\mathbf{x}, \mathbf{y}) = \rho_{\text{f}}(\mathbf{x}) \rho_{\text{f}}(\mathbf{y}) [h_{\text{dis}}(\mathbf{x}, \mathbf{y}) + 1]. \quad (25)$$

This relation becomes particularly simple for the PP systems, since the density factors are mere constants, in the whole volume of the homogeneous systems or in the fluid domain of the heterogeneous ones. Therefore, the overlap function is also straightforwardly determined by the short-range part of $h_{\text{dis}}(\mathbf{x}, \mathbf{y})$, that we now investigate.

B. The disconnected total correlation function

The theory of adsorption in disordered porous solids consists of a number of developments essentially based on cluster expansions and/or the use of the replica trick.^{53–64} Regarding the study of the disconnected total correlation function, most of them have been oriented towards the formulation of integral equation theories.⁷⁷

With respect to the PP systems, two models are of particular relevance.

On the one hand, as pointed out in Ref. 3, the homogeneous PP fluid systems are special cases of the templated-depleted systems put forward by Van Tassel *et al.*^{65–70} Indeed, in this class of models, the matrix samples are obtained by freezing equilibrium configurations of a binary mixture and by removing one component acting as a template for the other. Then, a fluid is introduced in the porous solid made of the remaining particles. One can easily figure out that, from this point of view, a homogeneous PP fluid system with pinning fraction x is nothing but a templated-depleted system built on an ideal binary mixture with matrix and template number fractions x and $1 - x$, respectively, in which the template particles are reinjected as the adsorbed fluid.

On the other hand, for the study of fluids adsorbed on substrates imposing amorphous boundary conditions at their surface, Dong *et al.* have considered a generic model in which the procedure for the preparation of the solid is a heterogeneous pinning process, but no assumption is made on the fluid in contact with it.⁵⁹ Again, it is clear that the heterogeneous PP systems are no more than a special instance of this setup.⁷⁸

For both models, their proposers have derived sets of Ornstein-Zernike (OZ) equations that must be adapted to the PP fluid systems by using the relations (9) and (15). In passing, one may note that in both cases, the last one of these relations implies that the disconnected total correlation function does not only describe the sample-to-sample fluctuations of the random one-body fluid density, as follows from Eqs. (19) and (25), but also quantifies the memory kept by the fluid of the positions occupied by the unpinning particles at the time of preparation of the substrate.

The results are very compact, as they reduce to only two linearly independent OZ equations. First, the one describing the original bulk system,

$$h(r) = c(r) + \rho c \otimes h(r), \quad (26)$$

comes out unchanged, with \otimes denoting a convolution in real space and $c(r)$ the direct correlation function. This is expected, since $h(r)$ and $c(r)$ actually have the status of input quantities for the problem at hand, stemming from a prior study of the structure of the bulk fluid from which the PP systems are prepared. Second, the disconnected correlation functions are found to obey

$$h_{\text{dis}}(r) = c_{\text{dis}}(r) + \rho c \otimes h(r) - (1 - x) \rho [c - c_{\text{dis}}] \otimes [h - h_{\text{dis}}](r) \quad (27)$$

for the homogeneous PP systems,³ and

$$h_{\text{dis}}(\mathbf{x}, \mathbf{y}) = c_{\text{dis}}(\mathbf{x}, \mathbf{y}) + \rho c \otimes h(|\mathbf{x} - \mathbf{y}|) - \rho \int d\mathbf{u} [c - c_{\text{dis}}](\mathbf{x}, \mathbf{u}) \chi_{\mathcal{R}}(\mathbf{u}) [h - h_{\text{dis}}](\mathbf{u}, \mathbf{y}) \quad (28)$$

for the heterogeneous ones, with $c_{\text{dis}}(r)$ [$c_{\text{dis}}(\mathbf{x}, \mathbf{y})$] the disconnected direct correlation function associated with $h_{\text{dis}}(r)$ [$h_{\text{dis}}(\mathbf{x}, \mathbf{y})$]. Using $\chi_{\mathcal{R}}(\mathbf{u}) = 1 - \chi_{\overline{\mathcal{R}}}(\mathbf{u})$, a structural similarity between both equations immediately appears, with $\chi_{\overline{\mathcal{R}}}(\mathbf{u})$ playing the role of a space-dependent pinning fraction. With Eq. (28), one can also remark the unusual situation of an inhomogeneous integral equation theory that does not require a computation of the density profile through an additional relation.⁷⁹

Further results of interest can be obtained by delving into the peculiar diagrammatic structure of the underlying cluster expansions.^{53–57,59}

From a general point of view, Madden's formalism dealing with arbitrary fluid-matrix ensembles shows that the diagrams contributing to the disconnected total correlation function involve many-body matrix distribution functions of all orders.^{54,80} Since in the PP systems these distribution functions coincide with those of the original bulk fluid, this observation nicely embodies the characterization of h_{dis} as a point-to-set correlation function probing the full many-body structure of this fluid. However, this aspect does not appear to play any particular role as the theory unfolds, so that the PP systems do not seem to occupy any special place in this framework.

The low pinning fraction regime of the homogeneous PP systems has recently been considered, with calculations of the leading order contribution to $h_{\text{dis}}(r)$ for small x .^{39,49} This result can be derived in the present framework with the help of the generic topological constraints on the diagrams contributing to $h_{\text{dis}}(r)$ and $c_{\text{dis}}(r)$ for any matrix ensemble. Indeed, they impose that, in the limit of the matrix density ρ_m going to zero, these functions are of order ρ_m and ρ_m^2 , respectively.⁸¹ Plugging this into Eq. (27), knowing that ρ_m means $x\rho$ and that $h(r)$ and $c(r)$ are of order 1 (remember that they simply refer to the bulk fluid from which the PP system is prepared), leads after simple manipulations to

$$h_{\text{dis}}(r) = x\rho h \otimes h(r), \quad x\rho \rightarrow 0, \quad (29)$$

a result that can be confirmed independently of Eq. (27) by a direct inspection of the diagrams contributing to $h_{\text{dis}}(r)$ at order ρ_m . If the limit $x\rho \rightarrow 0$ involves $\rho \rightarrow 0$, i.e., if homogeneous pinning in an extremely dilute gas is considered, $h(r)$ in this equation implicitly stands for $\lim_{\rho \rightarrow 0} h(r)$.

In the limit $x \rightarrow 0$ with ρ fixed, Eq. (29) expresses the linear response of the fluid to the homogeneous pinning constraint. Its derivation in Refs. 39 and 49 has been through *ad hoc* calculations especially tailored for the study of PP systems. By considering the problem in the general settings of the theory of adsorption, the present approach has the advantage that it lends itself to simple

generalizations. For instance, the above-mentioned diagrammatic inspection of $h_{\text{dis}}(r)$ shows that Eq. (29), with $x\rho$ replaced by ρ_m , generically describes the response of a fluid to a vanishingly small amount of randomly placed matrix particles identical to the fluid ones, irrespective of the detailed disordered structure of the matrix. Thus, not only has the contribution to $h_{\text{dis}}(r)$ reported in Eq. (29) little to do with point-to-set correlations, as argued in Refs. 39 and 49, but it is also completely unspecific of the PP systems.

The question of an analogous contribution in the heterogeneous case has been raised by some authors.^{34,49} It can be addressed along exactly the same lines as above, thanks to the cluster expansions of Ref. 59. Here, the asymptotic regime in which the perturbation due to the pinning is small corresponds to locations in \mathcal{R} far from any fluid-solid interface. The result is derived in the Appendix and reads

$$h_{\text{dis}}(\mathbf{x}, \mathbf{y}) = \rho \int d\mathbf{u} h(|\mathbf{x} - \mathbf{u}|) \chi_{\overline{\mathcal{R}}}(\mathbf{u}) h(|\mathbf{u} - \mathbf{y}|), \\ \mathbf{x}, \mathbf{y} \in \mathcal{R}, d(\mathbf{x}, \overline{\mathcal{R}}) \text{ and/or } d(\mathbf{y}, \overline{\mathcal{R}}) \rightarrow +\infty, \quad (30)$$

with $d(\mathbf{x}, \overline{\mathcal{R}}) = \min_{\mathbf{r} \in \overline{\mathcal{R}}} |\mathbf{x} - \mathbf{r}|$. The above-mentioned structural similarity between Eqs. (27) and (28) remains between Eqs. (29) and (30).

Assuming that the separate problem of the structure of the original bulk fluid is under control, an explicit calculation of h_{dis} beyond these asymptotic regimes in the framework of an integral equation theory requires an approximate closure of Eqs. (27) or (28), in the form of an additional independent relation involving c_{dis} and h_{dis} . A very convenient route towards such closures is the use of the replica trick.^{55–58}

In order to illustrate such a scheme with a simple numerical computation, we consider the homogeneous PP fluid systems prepared from the one-component hard-sphere fluid, in the so-called replica Percus-Yevick (PY) approximation.^{55–57,68,69} This closure implies that the structure of the bulk fluid is handled through the usual PY approximation, with a well-known analytic solution for the hard-sphere fluid,⁷¹ and that $c_{\text{dis}}(r)$ is identically set to zero.

The resulting disconnected total correlation function $h_{\text{dis}}(r)$ is displayed in Fig. 1 for representative values of the compacity of the original bulk system $\phi = \rho\pi\sigma^3/6$ (σ denotes the particle diameter) and of the pinning fraction x . There, $h_{\text{dis}}(r)$ is seen to have a perfectly regular short-distance behavior and to change smoothly with the parameters defining the PP system. Therefore, one can use its value at $r = 0$ as a direct proxy for the variations of the static overlap function.

Accordingly, the x -dependence of $h_{\text{dis}}(0)$ is shown in Fig. 2 for different values of ϕ . Here, we follow Ref. 38 and use the variable $x^{-1/3}$, as a reflection of the $(x\rho)^{-1/3}$ scaling of the typical distance between pinned particles.⁸² The replica PY $h_{\text{dis}}(0)$ is clearly seen to reproduce the qualitative behavior of the overlap function as measured

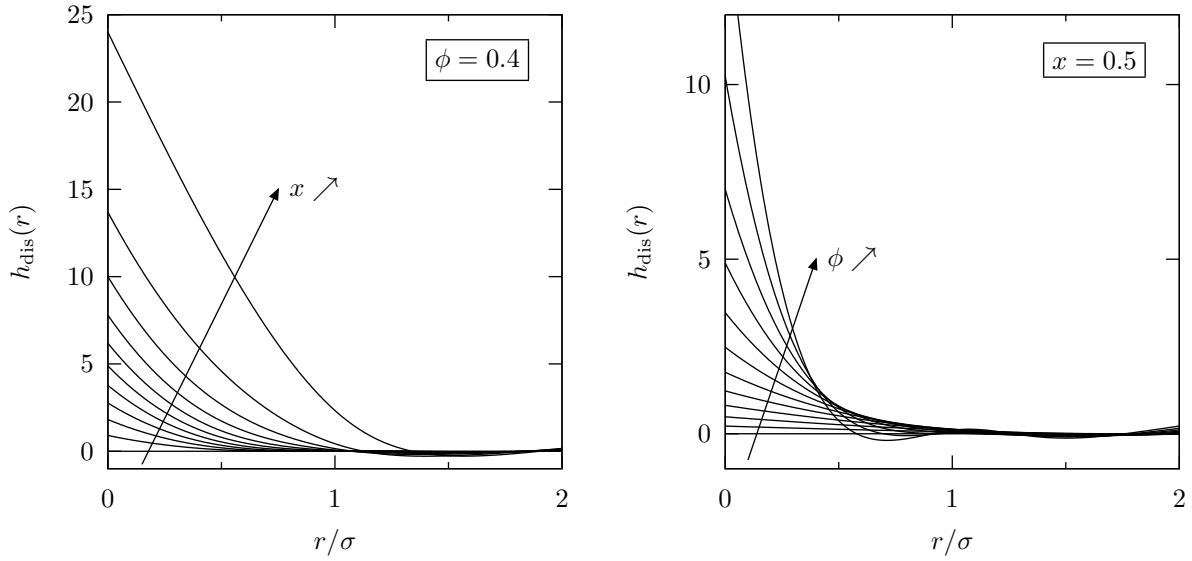


FIG. 1. Disconnected total correlation function $h_{\text{dis}}(r)$ of the homogeneous partly pinned hard-sphere fluid system, computed in the replica Percus-Yevick approximation. σ denotes the particle diameter, ϕ the compacity of the original bulk system, and x the pinning fraction. Left: $h_{\text{dis}}(r)$ as a function of x ($x = 0, 0.1, 0.2, \dots, 1$) for $\phi = 0.4$. Right: $h_{\text{dis}}(r)$ as a function of ϕ ($\phi = 0, 0.05, 0.1, \dots, 0.55$) for $x = 0.5$.

in computer simulations of dense hard-sphere mixtures, in particular, its rapid increase when x goes to one.^{38–40} Therefore, as in the simulation studies, it is possible with the present theory to pinpoint a moderately increasing density-dependent static lengthscale, by recording as a function of ρ the value of $(x\rho)^{-1/3}$ at which $h_{\text{dis}}(0)$ reaches some intermediate threshold value, e.g., $h_{\text{dis}}(0) = 10$, when x increases. This lengthscale cannot have any connection with glassiness, that is not captured by this theory (on the inability of the PY approximation to give a glass transition, see the appendix of Ref. 83). In passing, regarding the large x regime, it might be mentioned that an analytic expression for the terminal value of $h_{\text{dis}}(0)$ at $x = 1$ is provided by the present closure,

$$h_{\text{dis}}(0) = \frac{(1 + 2\phi)^2}{(1 - \phi)^4} - 1, \quad x = 1. \quad (31)$$

We close this part with Fig. 3, where the x -dependence of the replica PY $h_{\text{dis}}(0)$ is reported in a way that magnifies the departure from the linear response behavior, Eq. (29), when x grows from zero. At fixed $\phi \lesssim 0.4$, $h_{\text{dis}}(0)/(x\rho)$ is found to be an increasing function of x . This means in particular that the nonlinear contribution to $h_{\text{dis}}(0)$ is always positive in this low density regime. On the other hand, at fixed $\phi \gtrsim 0.4$, $h_{\text{dis}}(0)/(x\rho)$ first decreases then increases with x , hence develops a minimum that is more and more marked when ϕ grows. Therefore, in this moderate-to-high density regime, there is a sign change of the nonlinear contribution to $h_{\text{dis}}(0)$, from negative at low x to positive at high x . Obviously, these results should be taken with care because of the approximations underlying the replica PY closure, the neglect of $c_{\text{dis}}(r)$ of order $(x\rho)^2$, in particular. However, they

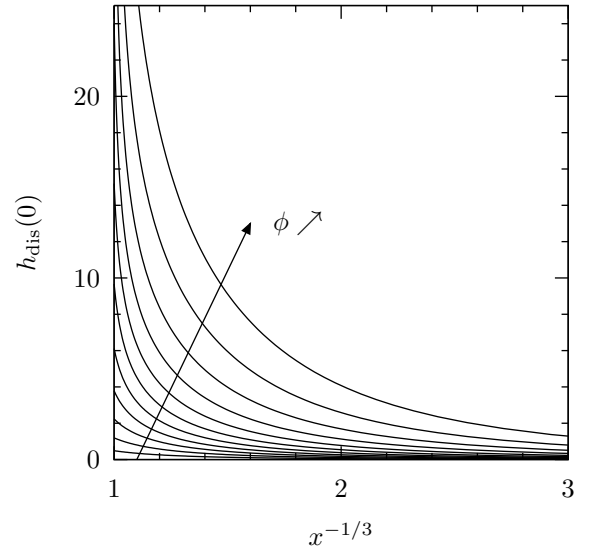


FIG. 2. Dependence on the pinning fraction x of the zero-separation value $h_{\text{dis}}(0)$ of the disconnected total correlation function of the homogeneous partly pinned hard-sphere fluid system, computed in the replica Percus-Yevick approximation. The compactities of the original bulk systems are $\phi = 0.05, 0.1, \dots, 0.55$.

should also serve as a reminder that, in principle, the behavior of the disconnected total correlation function, hence of the overlap, can undergo nontrivial qualitative changes unrelated to the physics of the glass transition.

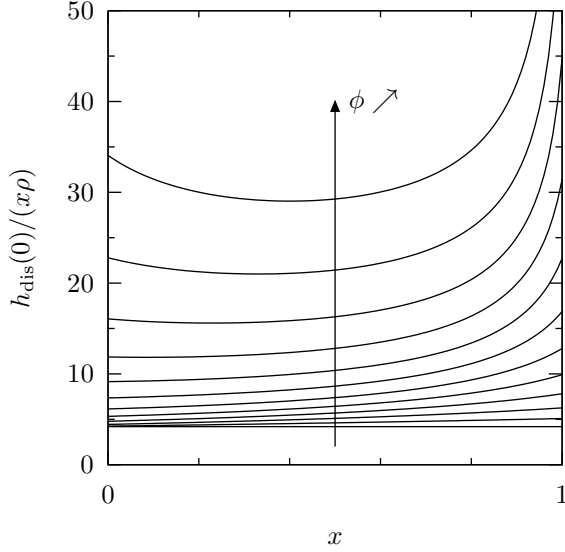


FIG. 3. Dependence on the pinning fraction x of the zero-separation value $h_{\text{dis}}(0)$ of the disconnected total correlation function of the homogeneous partly pinned hard-sphere fluid system, computed in the replica Percus-Yevick approximation. In order to magnify the departure from the linear response result, Eq. (29), with increasing x , $h_{\text{dis}}(0)$ is divided by $x\rho$. The compacities of the original bulk systems are $\phi = 0, 0.05, 0.1, \dots, 0.55$.

C. Discussion

We now contemplate the possible relevance of the above developments for the study of the PP systems prepared from glassforming liquids.

As long as the systems under consideration behave ergodically, i.e., as long as the global statistical-mechanical framework of Sec. II is appropriate, everything that has been said before remains valid. One deals with the same intricate measure of the interplay between the evolutions of the (many-body) correlations in a bulk fluid and its response to an externally imposed quenched disorder. Because of the lower temperatures and/or higher densities, the theoretical issue surely becomes more challenging, with uncertainties on the validity of the usual simple approximations,⁷¹ but the basic working equations such as the above OZ relations apply unmodified.

The situation changes when the possibility of broken ergodicity is introduced. This is the case in studies of PP systems whose aim is to probe a putative complex coarse-grained free-energy landscape characterizing the original bulk glassforming liquid and the related concept of an incipient amorphous order.^{24,31,32,34} Indeed, one of their central tenets is that a generic outgrowth of such a landscape will be the existence of many (meta)stable states accessible to the confined fluid.

One can easily devise how the previous formalism is altered in this case, borrowing ideas from the mean-field theory of glasses.^{5,84} To shorten the equations, we write $(N_m, \mathbf{q}^{N_m}) \equiv \mathbf{m}$ and $(N_f, \mathbf{r}^{N_f}) \equiv \mathbf{f}$. The relevant random

density field becomes state-dependent in addition to its realization-dependence and reads

$$\rho_f^\alpha[\mathbf{m}](\mathbf{x}) = \langle \hat{\rho}_f(\mathbf{x}; \mathbf{f}) \rangle_{\mathbf{m}}^\alpha, \quad (32)$$

where $\langle \dots \rangle_{\mathbf{m}}^\alpha$ denotes the realization-dependent thermal average inside state α . Its covariance defines a glassy disconnected two-point density,

$$\rho_{\text{dis}}^g(\mathbf{x}, \mathbf{y}) = \overline{\{\rho_f^\alpha[\mathbf{m}](\mathbf{x})\rho_f^\alpha[\mathbf{m}](\mathbf{y})\}_{\mathbf{m}}}, \quad (33)$$

where $\{\dots\}_{\mathbf{m}}$ represents the realization-dependent thermodynamically weighted average over the states and $\overline{\dots}$ still is the average over the matrix realizations. This expression can be reorganized by defining

$$\delta\rho_f^\alpha[\mathbf{m}](\mathbf{x}) = \rho_f^\alpha[\mathbf{m}](\mathbf{x}) - \{\rho_f^\alpha[\mathbf{m}](\mathbf{x})\}_{\mathbf{m}}, \quad (34)$$

so that

$$\rho_{\text{dis}}^g(\mathbf{x}, \mathbf{y}) = \overline{\{\rho_f^\alpha[\mathbf{m}](\mathbf{x})\}_{\mathbf{m}}\{\rho_f^\alpha[\mathbf{m}](\mathbf{y})\}_{\mathbf{m}}} + \overline{\{\delta\rho_f^\alpha[\mathbf{m}](\mathbf{x})\delta\rho_f^\alpha[\mathbf{m}](\mathbf{y})\}_{\mathbf{m}}}. \quad (35)$$

When the equilibrium consists of a collection of many metastable states with a finite configurational entropy, a remarkable feature of the mean-field theory leads to the equality $\{\rho_f^\alpha[\mathbf{m}](\mathbf{x})\}_{\mathbf{m}} = \rho_f[\mathbf{m}](\mathbf{x})$, i.e., the ergodic density profile in a given sample is recovered through state averaging. The first term in Eq. (35) is therefore $\rho_{\text{dis}}(\mathbf{x}, \mathbf{y})$, and one gets

$$\rho_{\text{dis}}^g(\mathbf{x}, \mathbf{y}) = \rho_{\text{dis}}(\mathbf{x}, \mathbf{y}) + \delta\rho_{\text{dis}}^g(\mathbf{x}, \mathbf{y}), \quad (36)$$

where $\delta\rho_{\text{dis}}^g(\mathbf{x}, \mathbf{y}) = \overline{\{\delta\rho_f^\alpha[\mathbf{m}](\mathbf{x})\delta\rho_f^\alpha[\mathbf{m}](\mathbf{y})\}_{\mathbf{m}}}$ is a kind of Edwards-Anderson or nonergodicity parameter for the PP system. By setting $\mathbf{x} = \mathbf{y} = \mathbf{x}_0$, where \mathbf{x}_0 is some convenient reference point, one obtains a *bona fide* point-to-set correlation function, $\rho_{\text{dis}}^g(\mathbf{x}_0, \mathbf{x}_0)$, essentially equivalent to the overlap, which would simply correspond to an integral of $\rho_{\text{dis}}^g(\mathbf{x}, \mathbf{y})$ over a small volume around \mathbf{x}_0 .

From Eq. (36), one immediately sees that, if there exists a contribution to the point-to-set correlation function originating in genuine glassy effects, it will typically come aggregated with a more commonplace one merely reflecting the (hypothetical) response of a normal fluid to the pinning disorder. On general grounds (see also Fig. 2), the latter contribution can be expected to grow stronger and longer-ranged as the density of the fluid increases and/or its temperature decreases, and, as stressed in the previous section with Fig. 3, although the underlying physics is somewhat simple, its behavior is not necessarily so. Such features might obscure or hide evolutions of the glassy contribution, which is usually the actual quantity of interest [for instance, the fact that the derivation of rigorous bounds between length and time scales requires the existence of some kind of Edwards-Anderson parameter^{5,25,27} clearly points towards a preeminent role of $\delta\rho_{\text{dis}}^g(\mathbf{x}_0, \mathbf{x}_0)$].

These observations suggest ways in which the toolbox of the theory of adsorption on random substrates

could be put to good use for the study of glassy PP systems. For instance, one could try to combine simulation data and theoretical predictions to correct the measured point-to-set correlation functions for the direct effect of adsorption, i.e., in terms of disconnected two-point densities, replace the analysis of $\rho_{\text{dis}}^g(\mathbf{x}_0, \mathbf{x}_0)$ by that of $\rho_{\text{dis}}^g(\mathbf{x}_0, \mathbf{x}_0) - \rho_{\text{dis}}(\mathbf{x}_0, \mathbf{x}_0)$. This could well turn out an unnecessary complication, if the glassy contribution is eventually shown to dominate, but it is also possible that no evidence for something like $\delta\rho_{\text{dis}}^g(\mathbf{x}_0, \mathbf{x}_0)$ is finally found. In any case, the current approach, in which no attempt is made to resolve two physically distinct contributions to the overlap, might not be optimal for sharp characterizations of the putative amorphous order developing in glassy systems.

IV. THE HOMOGENEOUS PARTLY PINNED LATTICE GAS

In this Section, we consider the outcome of the homogeneous pinning procedure when applied to a simple lattice gas, its equivalence with a peculiar instance of the random field Ising model (RFIM), and some possible consequences of this mapping.

A. Homogeneous pinning process in a lattice gas and mapping onto a random field Ising model

The pinning process described in Sec. IIA applies equally well if the particle positions are restricted to the vertices of a periodic lattice, i.e., if the simple fluid under consideration is actually a lattice-gas model. Thus, we might investigate along the same lines the most common member of this family, characterized by an infinite on-site exclusion preventing multiple occupancy of a lattice vertex and an attractive pair interaction $-w$ ($w > 0$) between particles located on nearest-neighbor sites.

As is well known, there are two ways to encode the configurations of such a lattice model. The first one is by simply keeping track of the particle positions, as with any other fluid model. The second one is specifically lattice-based and records, for each site i of the lattice, the number n_i of particles sitting on this site. For systems with infinite on-site exclusion, this occupancy number is a binary variable, $n_i = 0$ if the site is empty, $n_i = 1$ if it is occupied, easily mapped onto an Ising spin. Our first task is therefore to rephrase the results expressed in terms of particle positions in the language of occupancy variables.

The results for the bulk are very classic.⁸⁵ In terms of the variables $(n_1, n_2, \dots, n_V) \equiv \mathbf{n}^V$ (V now denotes the total number of sites), the grand-canonical statistical mechanics of the lattice gas is ruled by the effective Hamiltonian

$$H_{\text{bulk}}(\mathbf{n}^V) = -w \sum_{\langle ij \rangle} n_i n_j - \mu \sum_i n_i, \quad (37)$$

where $\langle ij \rangle$ generically denotes the nearest-neighbor pairs of sites, to which the first sum is restricted, and the chemical potential $\mu = k_B T \ln z$ has been introduced. Accordingly, the probability of a configuration \mathbf{n}^V reads

$$\mathcal{P}_{\text{bulk}}(\mathbf{n}^V) = \frac{e^{-\beta H_{\text{bulk}}(\mathbf{n}^V)}}{\Xi_{\text{bulk}}}, \quad \Xi_{\text{bulk}} = \sum_{\mathbf{n}^V} e^{-\beta H_{\text{bulk}}(\mathbf{n}^V)}. \quad (38)$$

The pinning process amounts to randomly choosing a fraction of the sites that are occupied in an instantaneous bulk configuration, to impose that they will remain so forever. This divides the lattice vertices into two complementary groups, those permanently hosting a matrix particle and those remaining accessible to the fluid particles, identified by the sets of indices $\{i_m\}$ and $\{i_f\}$, respectively. Therefore, a configuration \mathbf{n}^V after the pinning step naturally decomposes as $\mathbf{n}^{\{i_m\}} \oplus \mathbf{n}^{\{i_f\}}$, where $\mathbf{n}^{\{i_m\}} \equiv (n_i)_{i \in \{i_m\}}$ and $\mathbf{n}^{\{i_f\}} \equiv (n_i)_{i \in \{i_f\}}$, knowing that $n_i = 1$ for all $i \in \{i_m\}$ by construction. Then, noting that $N_m = \sum_{i \in \{i_m\}} n_i$ and $N_t = \sum_{i \in \{i_f\}} n_i$, the joint probability that a matrix realization labeled by $\{i_m\}$ is generated while the occupancy vector of the remaining sites is $\mathbf{n}^{\{i_f\}}$ follows from Eq. (3) as

$$\mathcal{P}_{\text{mt}}(\{i_m\}, \mathbf{n}^{\{i_f\}}) = \frac{e^{-\beta H_{\text{bulk}}(\mathbf{n}^{\{i_m\}} \oplus \mathbf{n}^{\{i_f\}}) + \ln(x) \sum_{i \in \{i_m\}} n_i + \ln(1-x) \sum_{i \in \{i_f\}} n_i}}{\Xi_{\text{bulk}}}, \quad (39)$$

from which the overall probability of the matrix configuration is obtained,

$$\mathcal{P}_m(\{i_m\}) = \sum_{\mathbf{n}^{\{i_f\}}} \mathcal{P}_{\text{mt}}(\{i_m\}, \mathbf{n}^{\{i_f\}}). \quad (40)$$

The effective Hamiltonian describing the confined fluid in a given matrix realization $\{i_m\}$ in terms of the variables $\mathbf{n}^{\{i_f\}}$ is retrieved from the argument of the exponential in Eq. (39) by removing all the pure matrix contributions, so that one gets

$$H_f(\mathbf{n}^{\{i_f\}} | \{i_m\}) = -w \sum_{\substack{\langle ij \rangle \\ i, j \in \{i_f\}}} n_i n_j - w \sum_{\substack{\langle ij \rangle \\ i \in \{i_f\}, j \in \{i_m\}}} n_i n_j - w \sum_{\substack{\langle ij \rangle \\ i \in \{i_m\}, j \in \{i_f\}}} n_i n_j - [\mu + k_B T \ln(1-x)] \sum_{i \in \{i_f\}} n_i, \quad (41)$$

where the condition $n_i = 1$ for $i \in \{i_m\}$ has not been explicitly used for later convenience.

In order to lift the restrictions on the sums in H_f , we take advantage of the fact that the physical properties of the system are left unaffected if a term independent of the fluid variables $\mathbf{n}^{\{i_f\}}$ is added to the Hamiltonian.⁸⁶ Thus, one can introduce the pure matrix contribution $-w \sum_{\langle ij \rangle; i, j \in \{i_m\}} n_i n_j - [\mu + k_B T \ln(1-x)] \sum_{i \in \{i_m\}} n_i$, consisting of the matrix-matrix interactions at the time

of pinning plus a suitable chemical potential term, and redefine

$$H_f(\mathbf{n}^{\{i_f\}}|\{i_m\}) = -w \sum_{\langle ij \rangle} n_i n_j - [\mu + k_B T \ln(1-x)] \sum_i n_i. \quad (42)$$

Note that this differs from the argument of the exponential in Eq. (39). This expression is in line with the picture of the PP systems as constrained systems, since the above Hamiltonian is the one of a mere lattice gas, in which occupancy of some sites is imposed.

Ising spin variables $\sigma_i = \pm 1$ are then readily introduced through the simple transformation $n_i = (1 + \sigma_i)/2$, which maps $H_f(\mathbf{n}^{\{i_f\}}|\{i_m\})$ onto

$$H_s(\boldsymbol{\sigma}^{\{i_f\}}|\{i_m\}) = -\frac{w}{4} \sum_{\langle ij \rangle} \sigma_i \sigma_j - \frac{1}{2} \left[\mu + \frac{qw}{2} + k_B T \ln(1-x) \right] \sum_i \sigma_i. \quad (43)$$

where q denotes the coordination number and irrelevant spin-independent contributions are omitted.

This Hamiltonian describes Ising variables evolving in the presence of permanently frozen up spins, $\sigma_i = +1$ for $i \in \{i_m\}$. Up to now, this freezing has been imposed by hand. However, it can be made a consequence of the Hamiltonian of the system, if an infinite on-site magnetic field forcing the spins to align is introduced, an idea that goes back to Grinstein and Mukamel in the context of the RFIM.⁸⁷ So, the present PP lattice gas is eventually shown to be equivalent to a RFIM, with the usual Hamiltonian

$$H_{\text{RFIM}}(\boldsymbol{\sigma}^V|\mathbf{h}^V) = -\frac{w}{4} \sum_{\langle ij \rangle} \sigma_i \sigma_j - \sum_i h_i \sigma_i, \quad (44)$$

and a random field realization

$$h_i = \begin{cases} \frac{1}{2} \left[\mu + \frac{qw}{2} + k_B T \ln(1-x) \right] & \text{if } i \in \{i_f\}, \\ +\infty & \text{if } i \in \{i_m\}. \end{cases} \quad (45)$$

In order to consider the mapping as complete, one might also wish to express the probability distribution of the random field configurations, as characterized by the sets of indices $\{i_m\}$, in terms of Ising spins. This only requires a rewriting of Eq. (40), leading to

$$\mathcal{P}_m(\{i_m\}) = \sum_{\boldsymbol{\sigma}^V} \left[\left(\prod_{i \in \{i_m\}} \delta_{+1, \sigma_i} \right) \times x^{\sum_{i \in \{i_m\}} \frac{1+\sigma_i}{2}} (1-x)^{\sum_{i \in \{i_f\}} \frac{1+\sigma_i}{2}} \mathcal{P}_{\text{Ising}}(\boldsymbol{\sigma}^V) \right], \quad (46)$$

with

$$\mathcal{P}_{\text{Ising}}(\boldsymbol{\sigma}^V) = \frac{e^{-\beta H_{\text{Ising}}(\boldsymbol{\sigma}^V)}}{\Xi_{\text{Ising}}}, \quad \Xi_{\text{Ising}} = \sum_{\boldsymbol{\sigma}^V} e^{-\beta H_{\text{Ising}}(\boldsymbol{\sigma}^V)}, \quad (47)$$

where $H_{\text{Ising}}(\boldsymbol{\sigma}^V)$ is the Ising Hamiltonian corresponding to $H_{\text{bulk}}(\mathbf{n}^V)$,⁸⁸

$$H_{\text{Ising}}(\boldsymbol{\sigma}^V) = -\frac{w}{4} \sum_{\langle ij \rangle} \sigma_i \sigma_j - \frac{1}{2} \left[\mu + \frac{qw}{2} \right] \sum_i \sigma_i. \quad (48)$$

Obviously, because of the direct correspondence between occupied cells ($n_i = 1$) and up spins ($\sigma_i = +1$), the same instance of the RFIM would be readily obtained if one would start with H_{Ising} and consider a pinning process acting on up spins only.

B. Discussion

A few comments can be made, based on these results.

A random pinning process in a particle system is found to be essentially equivalent to a spin pinning process restricted to up spins in an Ising model. As shown in Ref. 3, the former is accompanied by a change in activity and chemical potential, from z and μ for the original bulk fluid to $z(1-x)$ and $\mu + k_B T \ln(1-x)$ for the confined fluid, that originates in simple combinatorics.⁸⁹ This translates in the latter into a homogeneous shift of the external magnetic field in which the (unpinned) spins are plunged. This shift, equal to $k_B T \ln(1-x)/2$ and therefore negative, can be understood as a depolarizing field compensating for the fraction of pinned up spins. It is required to maintain the same average configurational properties in the bulk and pinned spin systems.

This fluid-like pinning scheme in the Ising model is clearly different from the usual obvious one, in which spins are frozen at random locations independently of their instantaneous value and no change of the external magnetic field is required. One can also map the latter onto a particle pinning scheme, through the correspondence between the Ising model and a lattice binary mixture.⁸⁵ However, in this case, the fluid model is incompressible and the pinning constraint acts on concentration rather than density fluctuations, so that one expects distinct physical consequences from this pinning scenario.

These observations raise the issue of the choice of a pinning scheme when one wants to investigate the effect of pinned particles on a fluid on the basis of a phenomenological model that can be very different from a fluid. Indeed, as found here for the simple Ising model, there might be more than just one possible pinning scheme, and choosing any particular one might not be innocent, since not all these schemes might be representative of an actual pinning process in a fluid system. In the absence of a guiding principle such as the above Ising model/lattice gas duality, a conservative strategy could then be to compare several schemes. To give a concrete example, Jack and Berthier⁵⁰ have investigated the effect of simple spin pinning on plaquette models that also admit a dual representation in terms of defect variables. It would maybe be interesting to consider the consequences of defect pinning as well.

Another way to write Eqs. (44) and (45) is

$$H_{\text{RFIM}}(\boldsymbol{\sigma}^V | \mathbf{h}'^V) = H_{\text{Ising}}(\boldsymbol{\sigma}^V) - \sum_i h'_i \sigma_i, \quad (49)$$

$$h'_i = \begin{cases} \frac{1}{2} k_B T \ln(1-x) & \text{if } i \in \{i_f\}, \\ +\infty & \text{if } i \in \{i_m\}, \end{cases} \quad (50)$$

where the Hamiltonian of the original bulk spin system appears perturbed by a random field term stemming from the pinning process. It turns out that this random contribution is very similar to the one seen in a RFIM built by Cammarota and Biroli in the framework of the RFOT theory.^{44,45} Both are indeed characterized by a homogeneous negative magnetic field, except at randomly placed sites where saturating positive fields fully polarize the spins in the up state.

In most respects, a direct comparison of these two results does not make sense, because of their very different theoretical foundations. The computer simulations performed by Cammarota and Biroli in order to benchmark the behavior of their model⁴⁵ might however represent an exception, because they are largely independent from the path followed for its derivation. Therefore, the existence of a preferred configuration corresponding to the one at the time of pinning, its stabilization by the pinning disorder, and the resulting dynamical coexistence between configurations that are similar to the reference one and configurations that are significantly different might be generic qualitative features of the PP systems, not necessarily tied to any particular underlying scenario.

V. CONCLUSION

In the recent years, a significant research effort has been invested in studies of partly pinned systems prepared from glassforming liquids. A strong motivation for this comes from a number of theoretical breakthroughs, suggesting that such studies have the potential to provide clear insight into pending issues of the physics of glassy systems. For instance, the theory of point-to-set correlations shows how PP systems could be used to detect the growth of otherwise elusive forms of “amorphous order” when approaching the glass transition.^{5,24–29} Another remarkable example is the prediction, within the RFOT theory, of an entropy-vanishing ideal liquid-glass transition in homogeneous PP systems that could be studied fully in equilibrium, at variance with the putative one in the bulk.^{44,45,51}

But, when a glassforming liquid is turned into a PP system, the pinning process does not only couple to its glassy properties. Physical phenomena already present in the PP systems deriving from normal fluid states and pertaining to the physics of adsorption on random substrates also come into play and blend with those related to glassiness.

The aim of the present work was to discuss this phenomena and to outline a reference framework allowing

one to take them into account in studies of glassy systems. Indeed, we believe, and we have provided arguments supporting this idea, that approaches systematically contrasting the behaviors of the glassy and normal PP systems should lead to sharper characterizations of the physics related to the glass transition than approaches only concentrating on the former.

This will require a better qualitative and quantitative knowledge of the properties of the normal PP systems than presently available. Indeed, these systems have been rather neglected in comparison to their glassy counterparts. The development of accurate integral equation theories based on closures of the Ornstein-Zernike equations (27) and (28) would be particularly interesting, because they could then be used to pinpoint the regime in which one needs to invoke new physics to explain the actual behavior of a dense PP fluid system. This will be the goal pursued in future work.

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Appendix A: Derivation of Equation (30)

In this Appendix, a simple derivation of Eq. (30) is outlined, based on standard arguments from the study of the asymptotic behavior of the correlation functions in simple fluids.⁷⁹

Using the decomposition

$$\begin{aligned} \rho c \otimes h(|\mathbf{x} - \mathbf{y}|) &= \rho \int d\mathbf{u} c(|\mathbf{x} - \mathbf{u}|) \chi_{\mathcal{R}}(\mathbf{u}) h(|\mathbf{u} - \mathbf{y}|) \\ &+ \rho \int d\mathbf{u} c(|\mathbf{x} - \mathbf{u}|) \chi_{\overline{\mathcal{R}}}(\mathbf{u}) h(|\mathbf{u} - \mathbf{y}|), \end{aligned} \quad (\text{A1})$$

Eq. (28) can be straightforwardly rewritten as

$$\begin{aligned} h_{\text{dis}}(\mathbf{x}, \mathbf{y}) &= c_{\text{dis}}(\mathbf{x}, \mathbf{y}) \\ &+ \rho \int d\mathbf{u} c(|\mathbf{x} - \mathbf{u}|) \chi_{\overline{\mathcal{R}}}(\mathbf{u}) h(|\mathbf{u} - \mathbf{y}|) \\ &+ \rho \int d\mathbf{u} c_{\text{dis}}(\mathbf{x}, \mathbf{u}) \chi_{\mathcal{R}}(\mathbf{u}) h(|\mathbf{u} - \mathbf{y}|) \quad (\text{A2}) \\ &+ \rho \int d\mathbf{u} c(|\mathbf{x} - \mathbf{u}|) \chi_{\mathcal{R}}(\mathbf{u}) h_{\text{dis}}(\mathbf{u}, \mathbf{y}) \\ &- \rho \int d\mathbf{u} c_{\text{dis}}(\mathbf{x}, \mathbf{u}) \chi_{\mathcal{R}}(\mathbf{u}) h_{\text{dis}}(\mathbf{u}, \mathbf{y}). \end{aligned}$$

For \mathbf{x} deep in the fluid region \mathcal{R} , the topological constraints on the diagrams contributing to c_{dis} and h_{dis} imply that the terms involving c_{dis} can be neglected. Indeed, the leading diagrams in c_{dis} are more connected in terms of fluid-matrix bonds than those in h_{dis} .⁷³ It follows that c_{dis} decays much faster than h_{dis} when the distance from the random substrate increases. Therefore, in this regime, one is left with

$$h_{\text{dis}}(\mathbf{x}, \mathbf{y}) \simeq \rho \int d\mathbf{u} c(|\mathbf{x} - \mathbf{u}|) \chi_{\overline{\mathcal{R}}}(\mathbf{u}) h(|\mathbf{u} - \mathbf{y}|) + \rho \int d\mathbf{u} c(|\mathbf{x} - \mathbf{u}|) \chi_{\mathcal{R}}(\mathbf{u}) h_{\text{dis}}(\mathbf{u}, \mathbf{y}). \quad (\text{A3})$$

One can also use Eq. (A1) in the OZ relation for the original bulk system, to get

$$h(|\mathbf{x} - \mathbf{y}|) = c(|\mathbf{x} - \mathbf{y}|) + \rho \int d\mathbf{u} c(|\mathbf{x} - \mathbf{u}|) \chi_{\mathcal{R}}(\mathbf{u}) h(|\mathbf{u} - \mathbf{y}|) + \rho \int d\mathbf{u} c(|\mathbf{x} - \mathbf{u}|) \chi_{\overline{\mathcal{R}}}(\mathbf{u}) h(|\mathbf{u} - \mathbf{y}|), \quad (\text{A4})$$

For \mathbf{x} deep in the fluid region \mathcal{R} , the last term is very small because of the factor $c(|\mathbf{x} - \mathbf{u}|)$ in the integrand, with \mathbf{u} constrained to be in $\overline{\mathcal{R}}$. So, one might approximate

$$h(|\mathbf{x} - \mathbf{y}|) \simeq c(|\mathbf{x} - \mathbf{y}|) + \rho \int d\mathbf{u} c(|\mathbf{x} - \mathbf{u}|) \chi_{\mathcal{R}}(\mathbf{u}) h(|\mathbf{u} - \mathbf{y}|). \quad (\text{A5})$$

Finally, Eqs. (A3) and (A5) can be recursively solved for $h_{\text{dis}}(\mathbf{x}, \mathbf{y})$ and $h(|\mathbf{x} - \mathbf{y}|)$, respectively. Comparing the two resulting infinite sums, one immediately recognizes

$$h_{\text{dis}}(\mathbf{x}, \mathbf{y}) \simeq \rho \int d\mathbf{u} h(|\mathbf{x} - \mathbf{u}|) \chi_{\overline{\mathcal{R}}}(\mathbf{u}) h(|\mathbf{u} - \mathbf{y}|). \quad (\text{A6})$$

Since $h_{\text{dis}}(\mathbf{x}, \mathbf{y})$ is invariant by exchange of its variables, it is obvious that this equation remains valid if it is \mathbf{y} and not \mathbf{x} that lies deep in the fluid region.

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- $$H_{\text{f}}(\mathbf{n}^V | \mathbf{u}^V) = -w \sum_{\langle ij \rangle} n_i n_j (1 - u_i)(1 - u_j) + n_i(1 - u_i)u_j + n_j(1 - u_j)u_i - [\mu + k_{\text{B}}T \ln(1 - x)] \sum_i n_i(1 - u_i). \quad (\text{A7})$$
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